

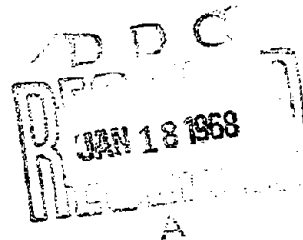
NRL Report 6617

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Flammability Properties of Hydrocarbon Fuels

Part 3 - Flammability Properties of Hydrocarbon Solutions in Air

November 21, 1967



NAVAL RESEARCH LABORATORY
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Part 3 - Flammability Properties of Hydrocarbon Solutions in Air

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*Fuels Branch
Chemistry Division*

November 21, 1967



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ABSTRACT

Previous work on the interrelations of the flammability properties on *n*-alkanes in air have been extended to both vapor and liquid fuel mixtures. Based on the application of Raoult's and Dalton's laws governing vapor pressure and composition above a solution of two or more liquid hydrocarbons to Le Chatelier's rule governing the flammability limits of vapor mixtures, equations have been derived which make it possible to predict overall flammability properties of mixtures from the properties and proportions of the individual components. The flammability properties which were studied include: lower and upper flammability limits, heat of combustion, stoichiometric concentration, flash point, and flammability index ("explosiveness"). The derived equations demonstrate, quantitatively, why vapor pressure of individual constituents plays a more important role than concentration on the overall flammability properties of liquid hydrocarbon solutions, and that a very small amount of a highly volatile contaminant in a relatively nonflammable fuel may make it flammable.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem C01-03
Projects SR 001-06-02-0600 and RR 010-01-44-5850

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FLAMMABILITY PROPERTIES OF HYDROCARBON FUELS

PART 3 - FLAMMABILITY PROPERTIES OF HYDROCARBON SOLUTIONS IN AIR

INTRODUCTION

As a result of contamination, improper preparation, or other reasons, less volatile, liquid combustibles may sometimes contain small quantities of highly volatile, flammable components, which can significantly influence the overall flammability properties of the mixture. It would be useful to be able to predict these and related effects quantitatively. Some physical properties of liquid solutions, such as density, are generally proportional to the properties and concentrations of the individual components. Combustion, on the other hand, occurs in the vapor phase; hence, flammability is a function of vapor concentration above the liquid. Therefore, it depends not only on the flammability properties and concentrations (both vapor and liquid), but also on the vapor pressures of the individual components of the solution to a marked degree.

From the standpoint of fire hazard in the storage and handling of flammable liquids and fuels, more knowledge is needed concerning the flammability properties of multi-component, liquid mixtures. The main goal of this work was to obtain a better understanding of the flammability properties of complex fuel mixtures -- particularly hydrocarbon fuels, such as gasoline, jet fuels, and diesel fuels. The flammability properties which will be discussed are lower and upper flammability limits, heat of combustion, stoichiometric concentration (oxidation), flash point, and flammability index (1,2).

PRINCIPLES INVOLVED

Le Chatelier's rule governing the flammability limits of vapor mixtures (3) and the useful rearrangement of this formula by Coward, et al. (4), have been known for a long time. These equations, which have been summarized by Coward and Jones (5) and, more recently, by Zabetakis (6), have been found to be applicable to hydrocarbon vapor mixtures (5-7) for both lower as well as upper flammability limits (5,7,8).

For liquid solutions it is first necessary to determine the vapor composition above the liquid before application of Le Chatelier's rule. Since hydrocarbon solutions do not deviate appreciably from Raoult's law (6,9), a combination of Raoult's and Dalton's laws govern vapor pressure and composition above a solution of two or more liquids. This treatment has been applied to lower flammability limits of liquid solutions containing methyl ethyl ketone and tetrahydrofuran by Zabetakis, et al. (10). Zabetakis (6) also reported its application to flammability limits of two-component liquid hydrocarbon mixtures. Empirical formulas, making use of certain of these concepts for calculating flash points of complex mixtures and blends, were reported by Thiele (11), Butler, et al. (12), and Mullins (13).

As a continuation of previous work at this Laboratory on the interrelations of the flammability properties of the n-alkanes in air (1,2), it was decided to extend some of the derived relationships to both vapor and liquid hydrocarbon mixtures, so as to be able to predict overall flammability properties from the properties and proportions of the individual components.

LIMITATIONS

The present discussion will be limited to liquid and vapor hydrocarbon fuels, excluding droplets and mists, in air at atmospheric pressure. It will be assumed that vapor is in equilibrium with the liquid at a given temperature and that vapor-air mixtures are uniform throughout. Except where otherwise stated, flammability limits, related properties, and vapor pressures are at 25 °C.

CHOICE AND HANDLING OF LITERATURE DATA

As a rule, a generalized approach will be taken, and symbols, rather than specific data, will be employed. Multicomponent solutions will be considered, but to illustrate some of the relationships, binary mixture systems will be given with solutions of *n*-alkanes in *n*-undecane as examples. Specific flammability data, where given, have been calculated from averaged literature data by means of the relationships which were described previously (1,2). Vapor pressure data and relationships are from standard sources (14-16).

FLAMMABILITY LIMITS OF VAPOR-AIR MIXTURES

Le Chatelier's rule (3) for a flammable vapor-air mixture of two or more components is

$$\sum_i (X'_i/L_i) = X'_A/L_A + X'_B/L_B + \dots = 1. \quad (1)$$

where X' is the actual vapor concentration, and L the concentration at the lower flammability limit (both expressed in percent by volume). The subscript i refers to the property in question of a general component, and A, B , etc., to that property of the specific components, A, B , etc., respectively. The equation, which is a simple additive relationship, states that for a mixture of gases to be at the lower flammability limit, the sum of the ratios of the actual concentration to that at the lower flammability limit for each constituent is equal to unity. By algebraic rearrangement, Coward, Carpenter, and Payman (4) derived a useful form of Le Chatelier's rule,

$$1/L_M = \sum_i (N'_i/L_i) = N'_A/L_A + N'_B/L_B + \dots \quad (2)$$

where N' is the mole fraction of a given fuel component in the total fuel vapor on an "air-free" basis, and the subscript M refers to the overall property of the mixture. Equation 2 expresses the lower flammability limit of the flammable vapor or gas mixture as a function of the sum of the ratios of the proportion of each component to that of its lower flammability limit.

Analogous expressions (5,7,8) can be used for the upper flammability limit U :

$$\sum_i (X'_i/U_i) = X'_A/U_A + X'_B/U_B + \dots = 1. \quad (3)$$

and

$$1/U_M = \sum_i (N'_i/U_i) = N'_A/U_A + N'_B/U_B + \dots \quad (4)$$

STOICHIOMETRIC CONCENTRATIONS OF VAPOR-AIR MIXTURES

A similar expression for stoichiometric concentration (assuming complete combustion to carbon dioxide and water) can be derived with the aid of previously derived relationships (1):

$$1/C_{SM} = \sum_i (N'_i/C_{Si}) = N'_A/C_{SA} + N'_B/C_{SB} + \dots \quad (5)$$

MOLAR HEAT OF COMBUSTION OF VAPOR-AIR MIXTURES

Le Chatelier's rule, which was developed from experimental considerations (3), can also be derived from molar heat of combustion (ΔH_m) concepts. It can be shown readily from energy considerations of a gas mixture that

$$\Delta H_{mM} = \sum_i (N'_i \Delta H_{mi}) = N'_A \Delta H_{mA} + N'_B \Delta H_{mB} + \dots \quad (6)$$

But as has been discussed previously (1,2), the molar heat of combustion is proportional to the reciprocal of the lower flammability limit. It has also been found that for hydrocarbons in general the constants of proportionality are approximately equal (17). Thus, $1/L$ can be substituted in Eq. (6), which, on canceling out the constants, becomes Eq. (2). This equation is Le Chatelier's rule.

VAPOR MIXTURES CONTAINING TWO FUEL COMPONENTS

For fuel-air mixtures containing only two fuel components, Eqs. (1) and (2) become

$$X'_A/L_A + X'_B/L_B = 1 \quad (7)$$

and

$$1/L_M = N'_A/L_A + N'_B/L_B \quad (8)$$

On rearrangement, Eq. (7) becomes

$$X'_B = L_B - (L_B/L_A) X'_A \quad (9)$$

Thus, for a lower limit mixture a plot of X'_B as a function of X'_A is a straight line (Fig. 1). Similarly, Eq. (8) may be rearranged, and by substitution of $(1 - N'_B)$ for N'_A (the sum of the mole fractions is unity), Eq. (8) becomes

$$1/L_M = (1/L_B - 1/L_A) N'_B + 1/L_A \quad (10)$$

Equation (10) is, likewise, linear. Thus, for a two-component fuel vapor-air mixture, for which the individual flammability limits are known constants, Eqs. (9) and (10) become simple linear equations which are useful for calculating or plotting concentrations of limit mixtures.

Analogous equations may be derived for the other flammability properties.

Examination of Eqs. (2), (4), (5), and (6) show that they are in the form

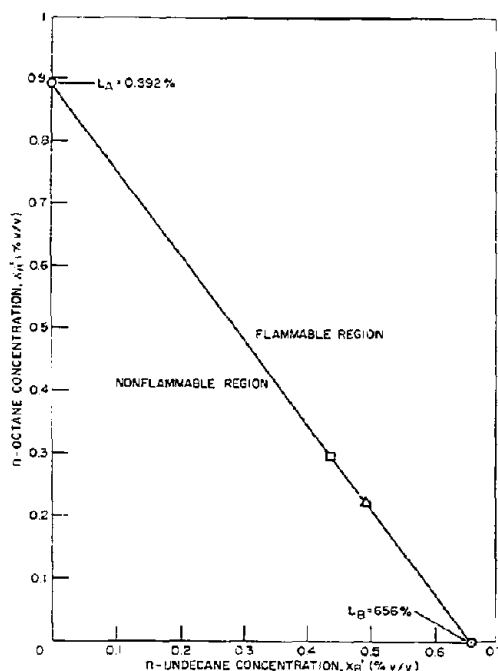


Fig. 1 - Theoretical lower flammability limits of binary fuel vapor components of n-octane and n-undecane in air

$$\Phi_M = \sum_i (N'_i \phi_i), \quad (11)$$

or for binary mixtures

$$\Phi_M = N'_A \phi_A + N'_B \phi_B, \quad (12)$$

where ϕ represents a generalized symbol for the various flammability properties $1/L$, $1/U$, $1/C_S$, and ΔH_m . The generalized equations analogous to Eqs. (9) and (10) are

$$X'_B = 1/\phi_B - (\phi_A/\phi_B) X'_A \quad (13)$$

and

$$\Phi_M = (\phi_B - \phi_A) N'_B + \phi_A. \quad (14)$$

Thus, since ϕ_A and ϕ_B are fixed flammability properties of the individual pure fuel components, both Eqs. (13) and (14) are straight line functions. The generalized flammability property functions of the mixture Φ_M (Eq. (14)) vary between the two extremes of the two components ϕ_A and ϕ_B , as is shown in Fig. 2. The magnitude of the variations differs, depending on the given properties. It would be useful to be able to compare these solution effects vs concentration for flammability properties of widely different magnitudes (for example, lower compared to upper flammability limits, both vs concentration)

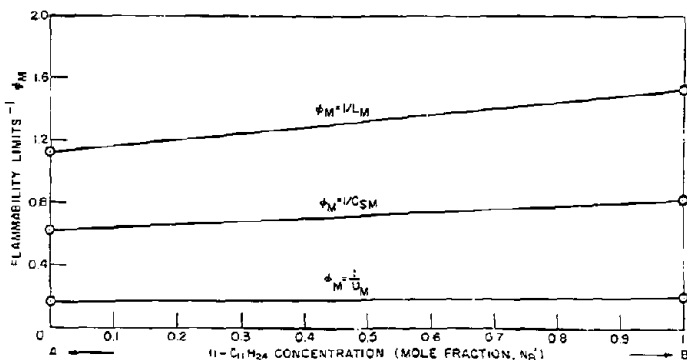


Fig. 2 - Theoretical flammability limits of binary fuel vapor mixtures of n-octane and n-undecane in air

or of different units (such as heat of combustion compared to lower flammability limits) or even against other physical properties. This comparison is possible by inventing a dimensionless, normalizing function Z for this purpose, where

$$Z = (\phi_M - \phi_A) / (\phi_B - \phi_A) . \quad (15)$$

Z represents the fraction of change (for a given property) of the mixture from A, relative to the total range between the two components. Thus, if $N_B^1 = 0$, $Z = 0$, and if $N_B^1 = 1$, $Z = 1$. By substitution of ϕ_M from Eq. (14), Eq. (15) becomes

$$Z = N_B^1 . \quad (16)$$

This relationship means that Z , a colligative property of the fuel vapor, is a function of its concentration. The Z -function will be found to be more useful in the discussion on liquid solutions which will follow.

FLAMMABILITY INDEX OF VAPOR-AIR MIXTURES

Another useful flammability property, which can be measured readily for a given fuel vapor-air mixture, has been referred to by various terms: "percent explosiveness," "explosivity," or "percent of the lower explosive limit" (2,18). This property, which has been discussed previously (2), is temperature-dependent, although it is usually expressed at 125°F. It is actually a measure of potential flammability hazard rather than "explosiveness" as such. For this reason the term "flammability index" is suggested as more descriptive of this property and will be used here. Regardless of the name given to it, this property is an expression of the fraction, or ratio, of the actual concentration of fuel vapor to that at its lower flammability limit. The fractions may be expressed as a decimal or percentage of volume concentrations, but the former, which is based on unity rather than 100, is simple and will be used as a basis of flammability units in the present discussion. If X_t^1 is the volume concentration of fuel vapor in equilibrium with the liquid at a given temperature t , and if L_t is the lower flammability limit (in v/v), then the flammability index E_t is defined as

$$E_t = X_t^1 / L_t . \quad (17)$$

Thus, if the fuel vapor concentration in a given air-fuel mixture is equal to the concentrations at the lower flammability limit ($X_t' = L_t$), the flammability index is unity ($E_t = 1$). If E_t is equal to or greater than unity, the mixture is flammable, provided it is not so large as to exceed the upper flammability value. If E_t is less than unity, the mixture is nonflammable. Le Chatelier's rule (Eq. (1)) is, therefore, a sum of ratios which are actually flammability indices. Thus, Eq. (1) becomes

$$E_M = \sum_i E_i = E_A + E_B + \dots = 1. \quad (18)$$

Therefore, the flammability index of a mixture is equal to the sum of the indices of the components.

From Eq. (18) it can be shown that lower-limit air mixtures, if mixed in any proportions, will give rise to mixtures which are also at their lower limits (5).

EFFECT OF TEMPERATURE ON FLAMMABILITY LIMITS OF VAPOR-AIR MIXTURES

Flammability limits of hydrocarbons do not vary significantly with moderate changes in temperature (5), but over a wide temperature range a correction for this variation must be made. Flammability limits of a hydrocarbon vapor-air mixture decrease approximately linearly with increasing temperature (1,2,5,6). The equation given by Zabetakis (6) will be used and can be put in the form

$$L_t/L = 1.02 - 0.000721t. \quad (19)$$

where L and L_t are the lower flammability limits at 25°C and $t^\circ\text{C}$, respectively. It will be convenient to write Eq. (19) in the form

$$L_t = QL. \quad (20)$$

where

$$Q = 1.02 - 0.000721t. \quad (21)$$

The question of the flammability limits of a multicomponent vapor-air limit mixture is treated by application of the temperature correction factor (Eq. (20)) to the rearranged Le Chatelier's formula (Eq. (2)). At any temperature t , Eq. (2) becomes

$$1/L_{Mt} = \sum_i (N_i'/L_{it}) = N_A'/L_{At} + N_B'/L_{Bt} + \dots \quad (22)$$

Substituting the value of L_t from Eq. (20) for each L_t in Eq. (22) and rearranging,

$$Q/L_{Mt} = \sum_i (N_i'/L_i) = N_A'/L_A + N_B'/L_B + \dots \quad (23)$$

By substituting $1/L_M$ from Eq. (2) for the right side of Eq. (23),

$$Q/L_{Mt} = 1/L_M; \quad (24)$$

which on rearranging becomes

$$L_{Mt}/L_M = Q. \quad (25)$$

Substituting the value of Q from Eq. (21), Eq. (25) becomes

$$L_{M1}/L_M = 1.02 - 0.000721t \quad (26)$$

Equation (26) is similar to Eq. (19); therefore, the flammability limits of a mixture vary with temperature in the same way as a single component fuel-air mixture.

The same relationships which have been demonstrated for lower flammability limits also apply to upper limits (5,7,8).

VAPOR COMPOSITION ABOVE THE LIQUID SOLUTION

Since hydrocarbon solutions obey Raoult's law (6,9), the vapor composition above a solution of hydrocarbons may be determined by a combination of Dalton's and Raoult's laws, i.e.,

$$N'_i = N_i p_i / \sum_i (N_i p_i) \quad (27)$$

where N'_i has been previously defined (Eq. (2)), p_i is the vapor pressure (atmospheres) of the pure liquid component i , N_i is its liquid concentration (mole fraction), and the summation term (denominator) is equal to the total vapor pressure.

The conventional textbook example (Fig. 3) of this ideal solution relationship for a two-component liquid solution usually plots the partial and total vapor pressures against concentration for two liquids of relatively similar vapor pressure. The top line (total pressure) is almost horizontal, forming what is approximately a rectangle with relatively equivalent diagonals representing the partial pressures of the individual solvents. In the case of binary liquid mixtures of two components of more widely different vapor pressures, the general shape of the graph is highly distorted from that of the textbook case, as is shown in Fig. 4 for a solution of *n*-octane and *n*-undecane. The graph demonstrates that the total vapor pressure of a liquid solution of volatile and relatively non-volatile components is approximately equivalent to the partial pressure of the more volatile constituents. This relationship has an important bearing on vapor composition and the flammability properties of liquid solutions.

FLAMMABILITY LIMITS OF LIQUID SOLUTIONS

By substitution of the right side of Eq. (27) for N'_i , Eq. (2) becomes the equivalent equations for liquid solutions:

$$1/L_M = \sum_i (N_i p_i / L_i) / \sum_i (N_i p_i) \quad (28)$$

or for a binary solution

$$1/L_M = (N_A p_A / L_A + N_B p_B / L_B) / (N_A p_A + N_B p_B) \quad (29)$$

This equation is plotted in Fig. 5 for three separate solutions of *n*-hexane, *n*-octane, and *n*-decane, each in *n*-undecane at 25°C. The curves in Fig. 5 also demonstrate the relatively large influence of the more volatile constituent. Analogous equations apply to upper flammability limits, stoichiometric concentrations, and molar heats of combustion.

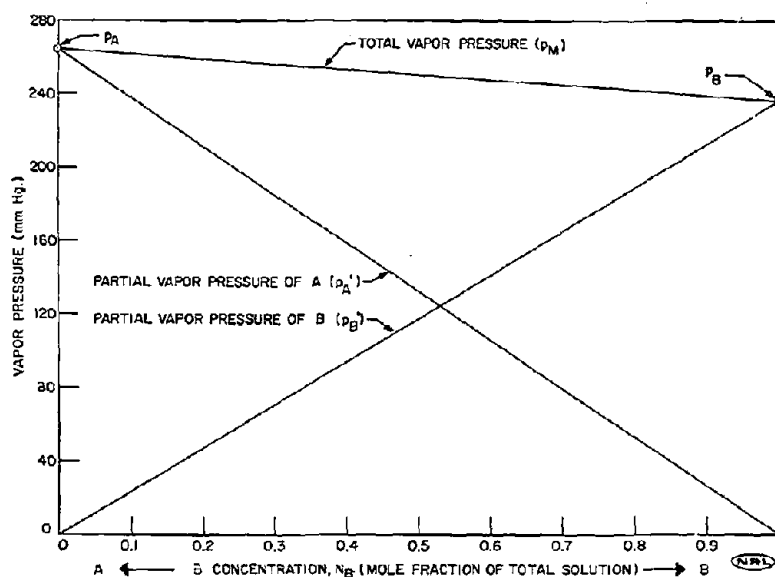


Fig. 3 - Vapor pressure vs concentration of ideal binary liquid solution

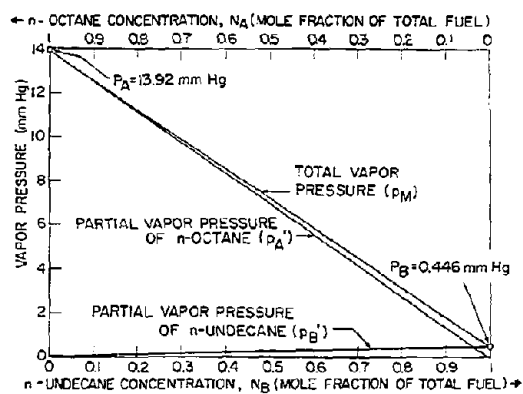


Fig. 4 - Vapor pressure vs concentration of binary liquid solutions of n-octane and n-undecane at 25°C

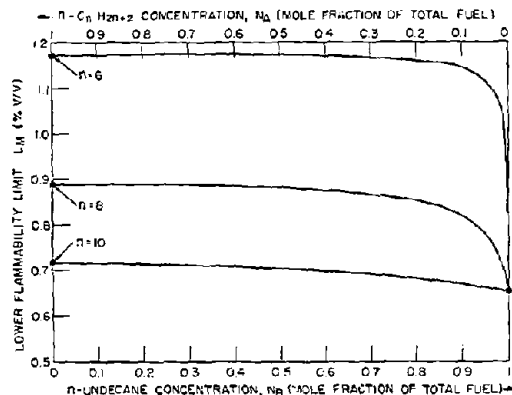


Fig. 5 - Theoretical lower flammability limits of binary liquid solutions of n-alkanes and n-undecane in air

BINARY LIQUID SOLUTIONS

The generalized function ϕ_M (analogous to Eq. (14) for vapor mixtures) for a liquid solution is

$$\phi_M = \frac{\sum_i (N_i p_i \phi_i)}{\sum_i (N_i p_i)} \quad (30)$$

and for a binary solution

$$\phi_M = (N_A p_A \phi_A + N_B p_B \phi_B) / (N_A p_A + N_B p_B) \quad (31)$$

Substituting the right side of Eq. (31) for ϕ_M in Eq. (15) and rearranging,

$$Z = N_B p_B / (N_A p_A + N_B p_B) \quad (32)$$

After expressing the reciprocal of Z as a function of the reciprocal of N_B and substituting $(1 - N_B)$ for N_A , Eq. (32) becomes

$$(1/Z) = (p_A/p_B)(1/N_B) + (p_B - p_A)/p_B \quad (33)$$

Thus, $1/Z$ is a linear function of $1/N_B$ (at constant temperature) with slope p_A/p_B and intercept $(p_B - p_A)/p_B$. Theoretical plots of Z vs N_B and $1/Z$ vs $1/N_B$ are given in Figs. 6 and 7, respectively, for binary liquid solutions of n-alkanes in n-undecane. In addition, a reciprocal type plot for some limited experimental data of Zabetakis, Cooper, and Furno (10) is given in Fig. 8. The graphs of both Figs. 7 and 8 are linear.

FLAMMABILITY INDEX OF LIQUID SOLUTIONS

The equilibrium vapor concentration in percent by volume X_i of a particular component of a liquid solution in the vapor space above the liquid is

$$X_i = 100 N_i p_i \quad (34)$$

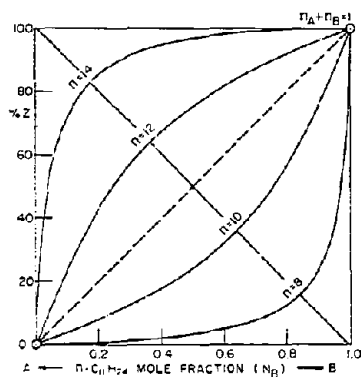


Fig. 6 - Theoretical Z values of binary liquid solutions of n-alkanes in n-undecane

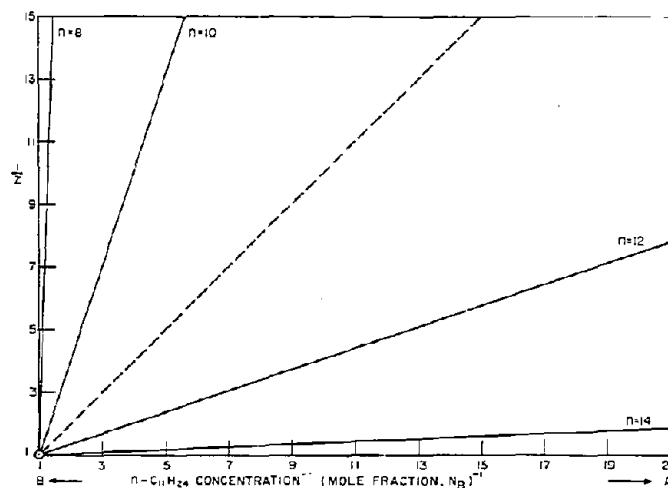


Fig. 7 - Reciprocal Z values vs reciprocal concentrations of binary liquid solutions of n-alkanes in air

where p_i is in atmospheres. By substitution of the value of x_i^l from Eq. (34), Eq. (17) (at temperature t) becomes

$$E_{it} = 100 N_i p_{it} / L_{it} \quad (35)$$

Similarly, substituting the value of E_{it} from Eq. (35) in Eq. (18),

$$E_{Mt} = \sum_i (100 N_i p_{it} / L_{it}) \quad (36)$$

But the flammability index of the vapors above a pure liquid component E_{it}^0 is

$$E_{it}^0 = 100 p_{it} / L_{it} \quad (37)$$

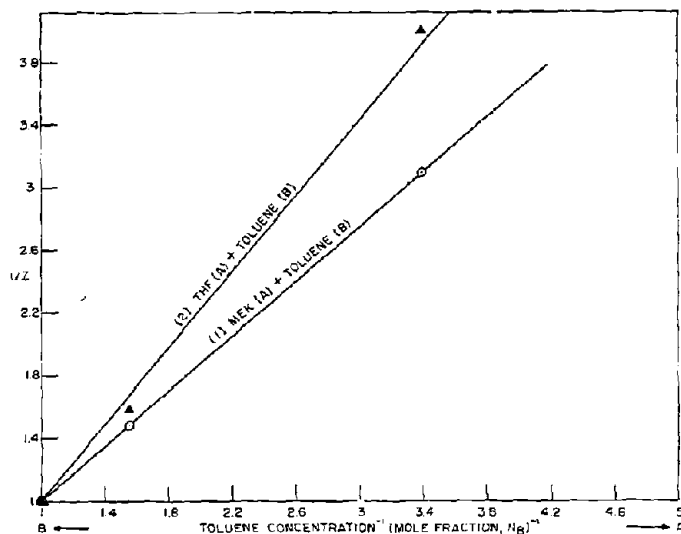


Fig. 8 - Reciprocal Z values vs reciprocal concentrations of binary liquid solutions of THF and MEK in toluene from experimental data of Zabetakis, Cooper, and Furno (10)

Substituting E_{it}^0 for its equivalent on the right side of Eq. (36),

$$E_{Mt} = \sum_i (N_i E_{it}^0) \quad (38)$$

For a binary solution

$$E_{Mt} = N_A E_{At}^0 + N_B E_{Bt}^0 \quad (39)$$

which on substituting $(1 - N_B)$ for N_A becomes

$$E_{Mt} = E_{At}^0 - (E_{At}^0 - E_{Bt}^0) N_B \quad (40)$$

Equation (40) is linear, as is shown in Fig. 9, which is a plot of the flammability indices (at 125°F, or 51.7°C) of several binary solutions of n -alkanes in n -undecane vs the concentration of n -undecane. The temperature is that of a standard test method (18). Both vapor pressure and flammability limits were calculated at 125°F to obtain the flammability indices. The horizontal line at E_M equal to unity delineates flammable from non-flammable solutions, and the n -alkane concentrations (N_A) needed to make n -undecane flammable at 125°F are indicated. A plot of N_A vs carbon number is indicated in Fig. 10. The two figures demonstrate that at higher vapor pressure, increasingly small concentrations of volatile components are required to make the relatively nonvolatile n -undecane flammable.

FLASH POINT

The concepts and meanings of flash point have been discussed previously (1). For these purposes we will accept the previous definition of flash point as that temperature

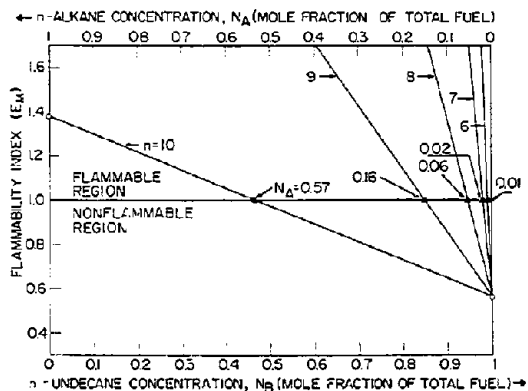


Fig. 9 - Flammability indices (explosiveness) of binary liquid solutions of n-alkanes and n-undecane in air at 125°F (51.7°C)

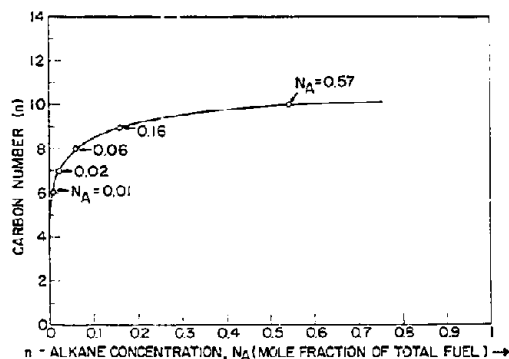


Fig. 10 - Flammable concentrations vs carbon number of binary liquid solutions of n-alkanes and n-undecane in air at 125°F (51.7°C)

at which the vapor pressure of the fuel gives an equilibrium concentration which is the concentration at the lower flammability limit. There are actually two flash point temperatures (1,2,6), i.e., a lower flash point t_L and an upper flash point t_U . The above definition defines t_L ; the upper flash point t_U may be defined in a similar manner, by upper flammability limit. These values are sometimes referred to as "lower and upper flammability limit temperatures." These concepts may be expressed graphically (1,2,6) as the intersections of the vapor pressure and the two flammability limit curves, both plotted against temperature.

For solutions of two or more flammable liquids the problem of defining these concepts is more complex. For solutions the lower flash point temperature is that temperature at which the vapor pressure of each of the flammable, volatile components is such

that the composition of the vapor-air mixture above the liquid is flammable, in accordance with Le Chatelier's rule. In the discussion up to this point the various flammability functions were assumed to be at constant temperature, and (except for flammability index) this temperature was 25°C. The concept of flash point brings in temperature as an additional variable.

For a flammable, multicomponent liquid solution at its flash point temperature t_{LM} the derived form of Le Chatelier's rule (Eq. (35)) becomes

$$\sum_i (100 N_i p_{i,t} / L_{i,t}) = 1, \quad (41)$$

where $p_{i,t}$ and $L_{i,t}$ are the vapor pressure and lower flammability limit values, respectively, of each component at the flash point temperature of the solution.

From Eq. (19)

$$L_{i,t} = (1.02 - 0.000721 t_{LM}) L_i, \quad (42)$$

where L_i is the lower flammability limit of a given fuel component at 25°C. Substituting the right side of Eq. (42) for $L_{i,t}$ in Eq. (41),

$$\sum_i \left[(100 N_i p_{i,t}) / (1.02 - 0.000721 t_{LM}) L_i \right] = 1 \quad (43)$$

which on rearranging becomes

$$\sum_i (N_i p_{i,t} / L_i) + 7.21 \times 10^{-6} t_{LM} - 0.0102 = 0. \quad (44)$$

For a two-component fuel Eq. (44) becomes

$$N_A p_{A,t} / L_A + N_B p_{B,t} / L_B + 7.21 \times 10^{-6} t_{LM} - 0.0102 = 0. \quad (45)$$

For a solution of pure hydrocarbon components of known concentrations N_i and assuming that the lower flammability limits of each fuel component L_i at 25°C are also known, it is then necessary to know the vapor-pressure-vs-temperature functions of each component $p_{i,t}$ in order to solve Eq. (44), or Eq. (45), for the flash point temperature t_{LM} . Vapor-pressure-vs-temperature data for the hydrocarbons are readily available (14-16). For purposes of this work the familiar Antoine type Eq. (15) was found to be a useful and good approximation:

$$\log_{10} p_{i,t} = b_i + M_i / (t_{LM} + C), \quad (46)$$

where b_i and M_i are constants, varying from hydrocarbon to hydrocarbon. In general, a value of 230 was found to be a good approximation for C for the n -alkanes. The values of b_i and M_i may be estimated from the literature (14-16). With values of b_i and M_i known for each fuel component, solution of Eq. (44) for t_{LM} can be attempted with the aid of Eq. (46). For approximate purposes this solution can be done graphically by the following elementary treatment.

From Eq. (44), let

$$Y = \sum_i \left[(N_i p_{i,t}) / (L_i) \right] + 7.21 \times 10^{-6} t_{LM} - 0.0102. \quad (47)$$

The solution involves finding its roots ($\gamma = 0$) which can be done graphically by plotting γ vs t_{LM} , at various values of t_{LM} . For each t_{LM} the value of p_{it} in Eq. (46) is determined and substituted in Eq. (47) for each component, which yields the solution for γ . This procedure was done for three separate binary solutions of *n*-hexane, *n*-octane, and *n*-decane, respectively, in *n*-undecane. The results are shown in Fig. 11. This figure also illustrates the large influence of higher volatile components in a flammable liquid solution.

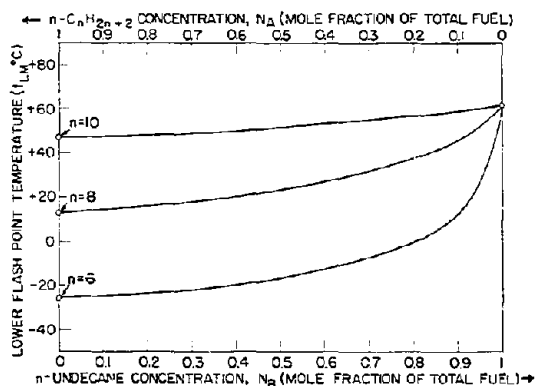


Fig. 11 - Theoretical lower flash-point temperatures of binary liquid solutions of *n*-alkanes and *n*-undecane in air

The combination of Eqs. (44) and (46) (eliminating p_{it}) expresses t_{LM} as a function of L_i , M_i , b_i , and N_i . It would be useful to be able to express t_{LM} as a function of the flash points of the individual pure components (t_{Li}) rather than that of the lower limits. This transformation was done by algebraic manipulation, which is summarized here.

For a pure liquid hydrocarbon at its flash point t_{Li} , Eq. (43) becomes, on rearranging,

$$100 p_{it}^0 / L_i = 1.02 - 0.000721 t_{Li} \quad (48)$$

where p_{it}^0 is the vapor pressure at t_{Li} . Solution of Eq. (48) for L_i gives

$$L_i = 100 p_{it}^0 / (1.02 - 0.000721 t_{Li}) \quad (49)$$

Substitution of Q_M and Q_i for the temperature terms in Eqs. (43) and (49), respectively, gives

$$\sum_i [100 N_i p_{it} / Q_M L_i] = 1 \quad (50)$$

and

$$L_i = 100 p_{it}^0 / Q_i \quad (51)$$

Substituting the value of L_i from Eq. (51) in Eq. (50) and simplifying,

$$\sum_i \left[(Q_i p_{i,t} N_i / Q_M p_{i,t}^0) \right] = 1, \quad (52)$$

where

$$Q_i = 1.02 - 0.000721 t_{Li}, \quad (53)$$

$$Q_M = 1.02 - 0.000721 t_{LM}, \quad (54)$$

$$\log_{10} p_{i,t}^0 = b_i + M_i / (t_{Li} + C), \quad (55)$$

and

$$\log_{10} p_{i,t} = b_i + M_i / (t_{LM} + C). \quad (46)$$

We now have a combination of five equations (Eqs. (46), (52)-(55)) by which we can express the lower flash point of the solution (t_{LM}) as a function of the flash points of the components (t_{Li}). By algebraic manipulation these five equations may be combined into a single equation. Subtraction of Eq. (55) from Eq. (46) gives

$$\log (p_{i,t} / p_{i,t}^0) = M_i (T'_{Li} - T'_{LM}) / T'_{Li} T'_{LM}, \quad (56)$$

where $T' = t + 230$.

Equation (52) may be rewritten as

$$\sum_i \left[(Q_i / Q_M) (p_{i,t} / p_{i,t}^0) N_i \right] = 1. \quad (57)$$

Substituting for the ratios Q_i / Q_M from Eqs. (53) and (54) and $p_{i,t} / p_{i,t}^0$ from the exponential form of Eq. (56), and using T' for temperature, Eq. (57) becomes

$$\sum_i \left\{ \left[(1642 - T'_{Li}) N_i / (1642 - T'_{LM}) \right] \times 10^{M_i (T'_{Li} - T'_{LM}) / T'_{Li} T'_{LM}} \right\} = 1. \quad (58)$$

The values in Fig. 11 were calculated by this equation and the results agreed with the graphical solution.

SUMMARY AND CONCLUSIONS

A theoretical study has been made of flammability properties of vapor and liquid multicomponent fuel mixtures in air, and mathematical equations have been derived which express these findings. The most important conclusion demonstrated by the derived equations is that a very small amount of a highly volatile contaminant in a relatively non-flammable fuel may make it flammable. Although precise relationships have been derived about relatively simple solutions of pure hydrocarbons, the concepts they imply are applicable to more complex mixtures, such as gasoline, jet and diesel fuels, and the like.

It would be interesting to investigate solutions which deviate appreciably from Raoult's law, especially those which might form azeotropes. Solutions with, for example, flash points below that of the lowest component would be of particular interest.

Experimental work is under way to test the theoretical equations.

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<p>Previous work on the interrelations of the flammability properties of n-alkanes in air have been extended to both vapor and liquid fuel mixtures. Based on the application of Raoult's and Dalton's laws governing vapor pressure and composition above a solution of two or more liquid hydrocarbons to Le Chatelier's rule governing the flammability limits of vapor mixtures, equations have been derived which make it possible to predict overall flammability properties of mixtures from the properties and proportions of the individual components. The flammability properties which were studied include: lower and upper flammability limits, heat of combustion, stoichiometric concentration, flash point, and flammability index ("explosiveness"). The derived equations demonstrate, quantitatively, why vapor pressure of individual constituents plays a more important role than concentration on the overall flammability properties of liquid hydrocarbon solutions, and that a very small amount of a highly volatile contaminant in a relatively nonflammable fuel may make it flammable.</p>		

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Hydrocarbon fuels Flammability Flammability limits Flash point Flammability index n-Alkanes Jet fuels Vapor pressure of fuel mixture Liquid fuel solutions Fuel vapor mixtures						